SHORT COMMUNICATIONS

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Structure refinement of bismuth oxide bromide, BiOBr.

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Abstract

$M_r = 304{\cdot}88$, tetragonal, $P4/nmm$, $a = 3{\cdot}9233\,(5)$, $c = 8{\cdot}105\,(2)$ Å, $V = 124{\cdot}7\,(3)$ Å^3, $Z = 2$, $D_m = 8{\cdot}082$, $D_x = 8{\cdot}12$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 825{\cdot}5$ cm^{-1}, $F(000) = 248$, room temperature; final $R = 0{\cdot}048$ for 190 independent observed reflections. The compound belongs to the BiOCl (PbFCl) layer structure family; its structure was refined in the course of a systematic study on crystal chemistry and bond relationships of the bismuth oxide halides. The Bi—O and Bi—Br bond lengths are 2·3251 (3) and 3·1698 (3) Å, respectively.

Transparent yellowish platelets of max. dimensions 2 × 2 × 0·5 mm were prepared by sublimation of commercial BiOBr powder in an evacuated quartz ampoule for 5 d from 983 to 943 K. A single crystal of size 200 × 10 × 5 µm was selected; value of D_m from Bannister & Hey (1935). Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, scan width 1·2°, ω–2θ scan mode, $2\theta < 70°$, h: −6 to 6, k: 0 to 6, l: 0 to 13; lattice parameters with program *GUINIER* (Carpentier, 1973), which corrected Guinier powder data using cubic As_2O_3 (a = 11·0765 Å) as internal standard, and refined with program *LSUCRE* (Evans, Appleman & Handwerker, 1963).

*SHELX*76 (Sheldrick, 1976) system; two standard reflections: no significant variation; 635 total reflections, 199 independent, 190 with $I > 3\sigma(I)$; $R_{\text{int}} = 0{\cdot}071$ (on F); corrections for Lorentz–polarization, absorption (transmission factors 0·05 to 0·66), and extinction [$g = 0{\cdot}6\,(1) \times 10^{-2}$] effects. As starting set of atom parameters the values of Bannister & Hey (1935), obtained from powder data, were chosen.

Refinement of positional and anisotropic thermal parameters resulted in final $R = 0{\cdot}048$,† $wR = 0{\cdot}045$ $\{w = 1/[\sigma^2(F) + 10^{-4}F^2]\}$, least squares based on F; 11 parameters refined; max. $\Delta/\sigma < 10^{-4}$; max. $\Delta\rho = 5{\cdot}5$, min. $\Delta\rho = -4{\cdot}7$ e Å^{-3} close to heavy atoms; scattering factors of neutral atoms (Cromer & Mann, 1968) used and corrected for anomalous dispersion (Cromer & Liberman, 1970). Atomic parameters are listed in Table 1, atom distances in Table 2.

Table 1. *Fractional atomic coordinates* (×10^4) *and anisotropic thermal parameters* (Å^2 × 10^2), $U_{12} = U_{13} = U_{23} = 0$, *with e.s.d.'s in parentheses*

	x	y	z	$U_{11} = U_{22}$	U_{33}
Bi	2500	2500	1540 (1)	1·07 (4)	0·81 (5)
O	2500	7500	0	1·1 (4)	0·6 (5)
Br	2500	2500	6568 (3)	1·38 (7)	1·0 (1)

Table 2. *Bond and shortest atom distances* (Å)

Standard deviations are in parentheses.

Bi—O	2·3251 (3) 4×	Bi—Br	3·1698 (3) 4×
Bi—Bi	3·7320 (5)	Br—Br	3·7625 (5)
O—O	2·7742 (2)	Br—O	3·4038 (6)

A systematic study on formation and structural properties of bismuth oxide halides reveals, besides well known compounds (*cf.* Sillén, 1941; Aurivillius, 1964; Wells, 1984), a number of new phases (Ketterer, 1985; Ketterer, Keller & Krämer, 1985).

Although phases with a ratio of Bi_2O_3:BiX_3 > 1:1 (X = I, Br, Cl) were of special interest, the bond lengths of the oxide bromides should be compared with those of the chemically and structurally simpler BiOBr; therefore, its structure was re-examined to confirm the atom distances determined 50 years ago from powder data (Bannister & Hey, 1935): both results show close agreement.

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42867 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Space group of octadecacarbonyl-1,2,3:4,5,6-bis-μ_3-[(η-toluene)cuprio]-*octahedro*-hexaruthenium. By

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Abstract

The structure of $(C_6H_5CH_3)_2Cu_2Ru_6(CO)_{18}$ should be described in $P\bar{1}$ and not in $P1$ as originally reported by Ansell, Modrick & Bradley [*Acta Cryst.* (1984), C**40**, 365–368].

During the preparation of a brief review (Jones, 1986) of noncentrosymmetric structures published in *Acta Crystallographica*, Section C, 1984, it was noticed that some structures were probably centrosymmetric. One such case is presented here.

The structure of the title compound was described by Ansell, Modrick & Bradley (AMB; 1984) in space group $P1$ with $Z = 2$; $a = 10{\cdot}236$, $b = 10{\cdot}395$, $c = 19{\cdot}267$ Å, $\alpha = 82{\cdot}64$, $\beta = 75{\cdot}27$, $\gamma = 82{\cdot}44°$. Inspection of AMB's atomic coordinates suggested strongly that both independent molecules in fact lay on centres of symmetry in $P\bar{1}$. Refinement of a centrosymmetric model, using the deposited structure factors and applying a coordinate shift of −0·985, 0·057, −0·003 from AMB's coordinates, confirmed this hypothesis. Details of refinement: 4357 observed reflections, unit weights, $R = 0{\cdot}039$, 272 parameters (*cf.* AMB's refinement; $R = 0{\cdot}038$, 495 parameters), max. Δ/σ 0·011, program system *SHELXTL* (Sheldrick, 1983). The increased stability of refinement in $P\bar{1}$ allowed the resolution of a twofold disorder of the toluene group of the second molecule; atoms C(1′)–C(7′), s.o.f. 0·64 (2), form the major component, and

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{iso}
Ru(1)	3168 (1)	4928 (1)	4774·2 (4)	25 (1)*
Ru(2)	4551 (1)	6956 (1)	5125·9 (5)	25 (1)*
Ru(3)	5907 (1)	5394 (1)	3924·2 (4)	25 (1)*
Cu(1)	3741 (1)	7098 (1)	3911 (1)	40 (1)*
O(1*a*)	2210 (9)	4391 (9)	3483 (5)	56 (2)
O(1*b*)	1779 (9)	2596 (9)	5564 (5)	55 (2)
O(1*c*)	452 (10)	6524 (9)	5154 (5)	57 (2)
O(2*a*)	1914 (10)	8677 (10)	5506 (5)	65 (3)
O(2*b*)	5138 (9)	7757 (9)	6457 (5)	56 (2)
O(2*c*)	5720 (9)	9368 (9)	4288 (5)	57 (2)
O(3*a*)	5049 (9)	4944 (9)	2590 (5)	55 (2)
O(3*b*)	8610 (9)	3829 (9)	3411 (5)	55 (2)
O(3*c*)	7130 (10)	7758 (10)	3025 (5)	65 (3)
C(1*a*)	2663 (12)	4638 (11)	3953 (6)	36 (3)
C(1*b*)	2390 (11)	3465 (11)	5289 (6)	35 (3)
C(1*c*)	1528 (11)	5988 (11)	5006 (6)	35 (3)
C(2*a*)	2902 (12)	7957 (12)	5340 (7)	42 (3)
C(2*b*)	4947 (12)	7359 (11)	5965 (6)	40 (3)
C(2*c*)	5292 (12)	8419 (11)	4569 (6)	39 (3)
C(3*a*)	5317 (11)	5114 (11)	3125 (6)	36 (3)
C(3*b*)	7574 (12)	4390 (11)	3656 (6)	38 (3)
C(3*c*)	6617 (12)	6886 (11)	3400 (6)	39 (3)
C(1)	3517 (14)	8197 (13)	2907 (7)	52 (3)
C(2)	3302 (14)	9266 (13)	3315 (8)	54 (3)
C(3)	1978 (13)	9688 (12)	3695 (7)	46 (3)
C(4)	890 (13)	9000 (12)	3668 (7)	48 (3)
C(5)	1129 (16)	7934 (15)	3270 (8)	64 (4)
C(6)	2431 (16)	7548 (15)	2894 (8)	64 (4)
C(7)	1702 (16)	10847 (15)	4132 (8)	65 (4)

Table 1 (*cont.*)

	x	y	z	U_{iso}
Ru(1′)	859 (1)	4948 (1)	8917·7 (4)	30 (1)*
Ru(2′)	−1916 (1)	5146 (1)	9828·0 (5)	31 (1)*
Ru(3′)	−39 (1)	6991 (1)	9904·7 (5)	31 (1)*
Cu(1′)	−1016 (2)	6908 (1)	8756 (1)	42 (1)*
O(1*a*′)	−194 (10)	4183 (10)	7706 (6)	63 (3)
O(1*b*′)	2373 (10)	6930 (9)	7834 (5)	59 (2)
O(1*c*′)	3247 (10)	2928 (10)	8506 (5)	62 (3)
O(2*a*′)	−4264 (11)	7277 (10)	10036 (6)	71 (3)
O(2*b*′)	−3802 (11)	3452 (10)	10885 (6)	72 (3)
O(2*c*′)	−3100 (11)	4376 (10)	8671 (6)	69 (3)
O(3*a*′)	1488 (11)	8993 (11)	8843 (6)	77 (3)
O(3*b*′)	958 (11)	8024 (11)	11045 (6)	74 (3)
O(3*c*′)	−2286 (12)	9187 (11)	10130 (6)	76 (3)
C(1*a*′)	146 (13)	4493 (12)	8201 (7)	46 (3)
C(1*b*′)	1757 (12)	6215 (11)	8265 (6)	39 (3)
C(1*c*′)	2347 (13)	3672 (12)	8716 (7)	44 (3)
C(2*a*′)	−3299 (14)	6520 (13)	9938 (7)	48 (3)
C(2*b*′)	−3005 (13)	4078 (12)	10506 (7)	47 (3)
C(2*c*′)	−2569 (13)	4709 (12)	9083 (7)	48 (3)
C(3*a*′)	897 (13)	8161 (13)	9223 (7)	49 (3)
C(3*b*′)	593 (13)	7521 (13)	10632 (7)	47 (3)
C(3*c*′)	−1484 (13)	8292 (13)	10025 (7)	48 (3)
C(1′)	−1035 (9)	8481 (17)	7885 (9)	37 (5)
C(2′)	−1825 (9)	9472 (17)	8273 (9)	47 (5)
C(3′)	−3235 (9)	9480 (17)	8478 (9)	43 (5)
C(4′)	−3854 (9)	8497 (17)	8296 (9)	65 (7)
C(5′)	−3064 (9)	7506 (17)	7907 (9)	60 (7)
C(6′)	−1654 (9)	7498 (17)	7702 (9)	48 (6)
C(7′)	−4049 (30)	10591 (29)	8976 (16)	86 (9)
C(1″)	−2571 (42)	9745 (22)	8423 (16)	54 (6)
C(2″)	−3660 (42)	9054 (22)	8442 (16)	54 (6)
C(3″)	−3432 (42)	7888 (22)	8122 (16)	54 (6)
C(4″)	−2115 (42)	7414 (22)	7784 (16)	54 (6)
C(5″)	−1026 (42)	8105 (22)	7765 (16)	54 (6)
C(6″)	−1253 (42)	9271 (22)	8085 (16)	54 (6)
C(7″)	−5049 (39)	9684 (37)	8757 (21)	54 (6)

* Equivalent isotropic *U* calculated from anisotropic *U*.

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